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Coverage Dependent Disorder-to-Order Phase Transformation of an Uracil-Derivative on Ag(111)

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ABSTRACT. The self-organization of an angular bis(uracil-ethynyl) benzene derivative is investigated on Ag(111) by means of scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions. It is found - starting at low submonolayer coverage - that upon increasing the molecular coverage a disorder-to-order phase transformation occurs. Specifically, at low and intermediate molecular coverage a glassy phase consisting of one dimensional (1D) chains and 2D aggregates is observed, while close to a first complete molecular layer, a well-ordered 2D close-packed phase is revealed. The main driving forces responsible for the structure formation are: (i) the high self-complementarity of the uracil (**U**) moiety, resulting in **U**-**U** homopairs through twofold C=O···H–N H-bonds; (ii) the steric hindrance induced in the system by the alkyl chains. The delicate balance between the molecule-molecule and the molecule-substrate interactions leads to a complex phase behavior of the uracil derivative at the solid-vacuum interface. On the basis of this detailed study, we present a qualitative understanding of the peculiar phase behavior of the system.

KEYWORDS: STM, uracil, hydrogen bonds, phase transformation, self-assembly.

INTRODUCTION

Supramolecular self-assembly at interfaces has proven to be a powerful means for fabricating functional nanomaterials by employing specially designed molecules as building blocks.[1,2] Molecules with well-defined shapes and engineered interactive sites able to participate in strong directional interactions are particularly attractive for the engineering of functional surfaces. Supramolecular recognition motifs based on hydrogen bonding interactions are among the most commonly used due to their selectivity, directionality and reversibility. An example of a H-bonding recognition site is uracil (**U**), (Figure 1a, black dashed circle) a RNA nucleobase, intensively studied not only because of its importance in biological interactions,[3] but also because of its possible nanotechnological applications.[4] **U**, due to its imidic group (CO–NH–CO), presents both H-bond acceptor (CO) and H-bond donor (NH) sites manifesting a high ability to self-assemble through weak homo-complementary double H-bonding interactions with the simplest structure formed being the **U** homopair. In the crystal structure, **U** assembles in a centrosymmetric dimer configuration with two C=O···H–N H-bonds arranged in planar sheets parallel to the (001) surface (Figure S1, Supporting Information (SI)).[5]

Monolayers of **U** were first observed at the mercury-water interface using electrochemical methods.[6,7] More recently, electrochemical studies of monolayers of **U** have also been performed on solid electrodes with well-defined crystallographic orientations. Here, scanning tunneling microscopy (STM) experiments contributed enormously to the understanding of the self-arrangements of **U** within the monolayer. One of the first reports puts the focus on **U** on MoS_2, and on highly oriented pyrolytic graphite (HOPG) where the molecules form dimers arranged in a herringbone pattern.[8] For **U** adsorbed on the Au(hkl) electrode, highly ordered 2D physisorbed as well as chemisorbed adlayers were found in dependence of the applied potential at the

electrode.[9-11] Within the monolayer, the configuration of **U** and the intermolecular H-bonding are very similar to previous findings.[6-8] **U** adsorbed onto Ag(111) electrodes undergoes a 2D disorder-to-order phase transition.[12] For the ordered phase, chains of parallel flat **U** molecules held together through H-bonds were reported.

At the solid-vacuum interface, fewer studies involving the **U** group have been reported so far. On Cu(111), at low coverage, isolated trimers are observed, and at increased coverage, 2D islands with a hexagonal superstructure are formed.[13,14] Woodruff and coworkers reported that on Cu(110), **U** preferably binds to the surface through its imidic function by tilting its molecular plane perpendicular to the substrate and by aligning along the close-packed $[1\bar{1}0]$ azimuth.[15] On Ag(111) surfaces, **U** is adsorbed flat and in its intact form, and self-assembles in a close-packed arrangement through **U** homopairs.[16]

High interest was shown for the **U** moiety to be used as a functional building block to create functional nanostructures on surfaces through molecular recognition.[17,18] The adsorption of **U** derivatives on solid surfaces has been studied not only for understanding their physical and chemical properties, but also for potential applications in various domains of science and technology. **U** derivatives were synthesized with additional functionalities and were successfully applied in the construction of 1D and 2D structures on surfaces at the solid-liquid[19-24] and at the solid-vacuum interface.[25] In the latter work,[25] a di-uracil linear linker which has the **U** groups connected to a 1, 4-disubstituted central phenyl ring (positioned 180° with respect to each other) was assembled with a complementary linear di(acylamino)pyridyl linker to form 1D linear H-bonded arrays on Ag(111).

For the current study, an angular di-**U** derivative (1,2-Bis [(1-hexylurac-6-yl)] ethynylbenzene (**1**), (Figure 1a)), possessing two **U** groups now attached to a 1, 2-disubstituted central phenyl

ring (positioned 60° with respect to each other), was designed and synthesized (see SI) to explore the geometrical effect on the self-assembled network imposed by the substitution pattern on the central benzene ring. Specifically, in this paper we discuss the self-assembly of bisuracyl derivative **1** on Ag(111) as a function of coverage. In particular, we investigate how the molecular coverage alters the balance between molecule-molecule and molecule-substrate interactions, which are ultimately responsible for the structure formation of **1** on Ag(111).

EXPERIMENTAL METHODS

The experiments were performed in an ultrahigh vacuum (UHV) system (base pressure in the low 10^{-10} mbar region) consisting of different chambers for sample preparation and characterization. The Ag(111) single crystal was prepared by repeated cycles of Ar^+ bombardment and subsequent annealing at 700 K in order to obtain an atomically flat surface (monoatomic terraces of around 100 nm width). The molecules were deposited onto the surface (held at room temperature (rt)) by thermal evaporation from a quartz crucible heated at 470 K using a commercial 3-cell evaporator (Kentax UHV equipment). The deposition rate was controlled by a quartz crystal microbalance. The samples were analyzed with a commercial low temperature STM (Omicron Nanotechnology GmbH) at 77 K, unless stated otherwise. One monolayer (1ML) of **1** corresponds to a surface completely covered by the densest arrangement possible of **1**. The constant current images were obtained with a PtIr tip and the bias voltages are given with respect to a grounded tip. The free software WSxM[26] was used for the data processing of the STM images. The principal substrate directions were obtained from atomic resolution STM images of the clean Ag(111) surface. All lateral dimensions reported are valid within an accuracy of <10%. The synthesis of **1**, achieved through a series of Sonogashira-type Pd-catalyzed cross coupling reactions, is thoroughly described in the SI.

RESULTS/DISCUSSION

Molecule **1** (Figure 1a), as previously mentioned, has two **U** groups attached to a central aromatic ring through ethynyl spacers with an angle of 60°. Each **U** moiety is functionalized with a hexyl chain (at position 1, as labeled in Figure 1a) leaving only the imidic group CO–NH–CO (which corresponds to the labeled positions 2, 3 and 4 in Figure 1a) available for H-bonding interactions. An important feature of this molecule is the variability of the angle enclosed by the ethynyl arms (pink arrow, Figure 1a). As a consequence, the angle between the ethynyl linkers can deviate from the ideal value of 60°, distorting the 2-fold symmetry of the molecule (Figure S1, SI).[27] Furthermore, this flexibility can contribute to the optimization of the intermolecular interactions.

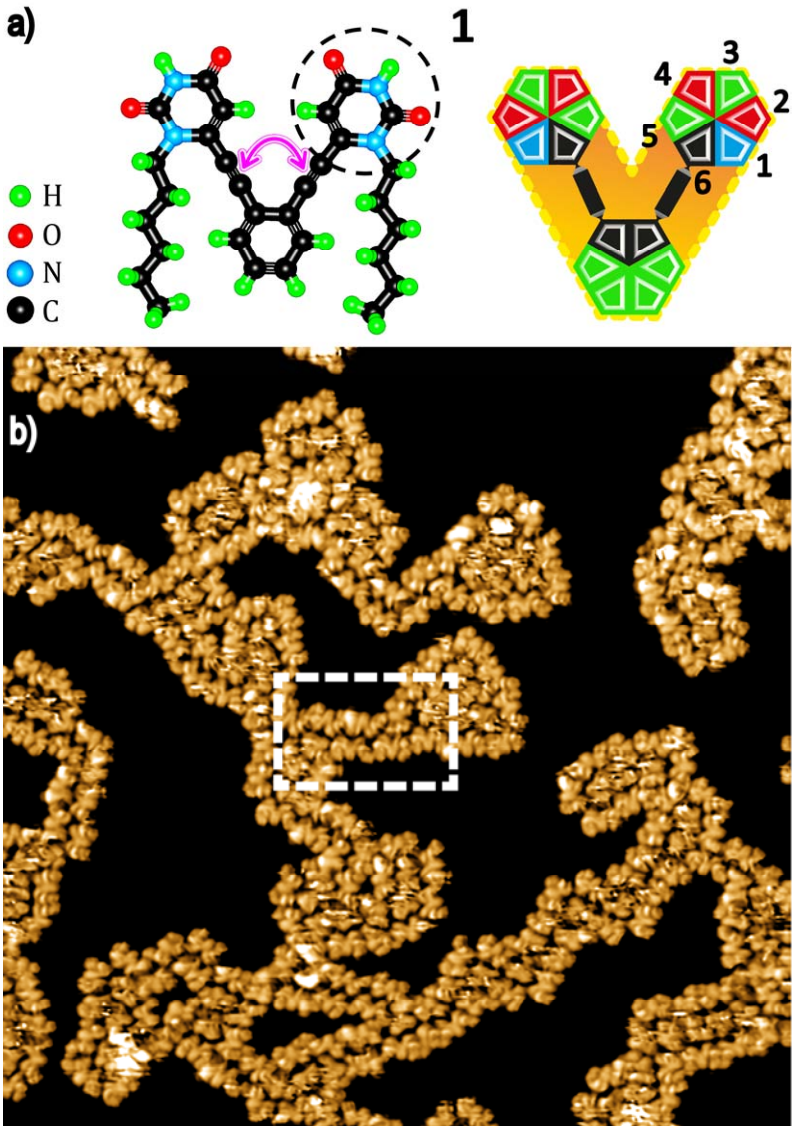

Figure 1. (a) Ball and stick model (left) of **1** and its schematic representation (right). For the right **U** moiety (encircled by a black dashed line) the atoms are numbered. The pink arrow indicates the variability of the angle enclosed by the ethynyl arms. (b) STM image (30 × 30 nm^2, V_t =1.5 V, I_t = 21 pA) for a coverage of ~0.65 ML of **1** on Ag(111) showing the formation of amorphous structures made up from double rows and clusters. The area marked by the dashed white rectangle is shown in detail in Figure 2.

When deposited on the Ag(111) surface, at room temperature and submonolayer coverage, molecules **1** are found in a 2D mobile phase (2D fluid). In order to minimize the surface mobility of **1** on the Ag(111) surface, the samples were cooled down to 77 K for imaging.

For coverages < 0.2 ML, short segments of 1D chains (double row structures) decorate the metal terraces. Such a structure is indicated by the white rectangle in Figure 1b, and presented in detail in Figure 2 (see also Figure S2, SI). The chains develop in a rather linear fashion on a short distance (~ few molecules) after which a kink induces a change of the chain direction (Figures S2 and S3a, SI). As can be seen in Figure 2, the 1D chain structure consists of double rows of molecules **1**. Within the structure, a single molecule **1** can be clearly identified. The three rings of **1**, adsorbed flat on the surface,[16] give rise to a V-shape appearance of the inner aromatic part of the molecule in the STM image, with the benzene ring at the vertex, at which the two **U** groups are attached through the ethynyl spacers. The hexyl chains appear as lateral curled wings what results in an overall M-shape appearance of the molecule.

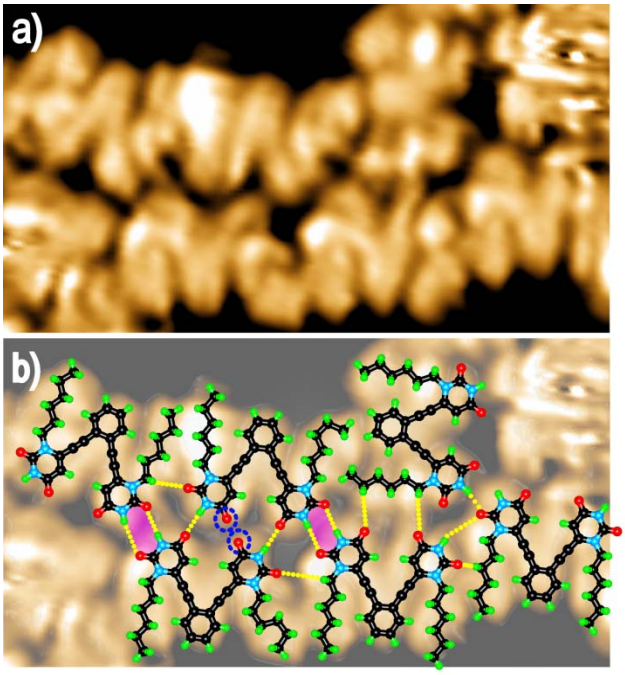

Figure 2. Bonding geometries observed for the double row structures. (a) High-resolution STM image (5.5×3 nm^2, V_t = 1.5 V, I_t = 100 pA) of the area marked by the dashed white rectangle in Figure 1b. The molecular arrangement within a double row can be seen in detail. (b) Proposed molecular model superimposed on the STM image shown in (a). The dotted yellow lines indicate the H-bonds formed between the molecules while the blue dashed circles indicate the repulsive interaction between the O atoms of neighboring molecules. The areas highlighted in pink point to double H-bonds formed between **U** moieties (which lead to the formation of the centrosymmetric **U** dimer) of neighboring molecules.

The molecules within one molecular row are oriented parallel to each other and rotated 180° with respect to the units in the adjacent row. In this configuration, the molecules within the double row structure are always oriented with their **U** groups (active H-bonding sites) pointing inside in order to facilitate H-bonding. A proposed model of the bonding geometries within the double row structure is shown in Figure 2b (H-bonds are represented by dotted yellow lines). Within the double row superstructure, each molecule **1** interacts asymmetrically with four neighbors having only one **U** involved in **U** dimerization[5-12,16,19,22,23,25,28-31] through two identical C=O(2)···H(3)–N H-bonds (the area highlighted in pink in Figure 2b). The O(4) atom of the **U** moiety involved in the homopair formation is involved in a single H-bond with the H(3) atom belonging to a molecule from the adjacent row (C=O(4)···H(3)–N). The second **U** moiety of the same molecule shares two single H-bonds (at positions 2 and 3): one with another **U** group and the second one with a C-H bond of the hexyl chain of a neighboring molecule.

With a systematic increase in coverage up to ~0.8 ML, in addition to the previously discussed double row structures, the formation of clusters was observed. Within the 2D amorphous structures, clusters with a triangular shape were observed on the surface. A closer analysis of

such triangular clusters (Figure S6, SI) reveals that on each side of the triangle molecules **1** are oriented parallel with respect to each other, and with the **U** groups pointing towards the inside of the cluster. Mostly, the molecular distribution along the sides of such an amorphous structure is similar to the one in the double row structure while the inner part of the triangular structure (or of any 2D aggregate) is fuzzy. The fuzziness in the STM images is attributed to the mobility of the alkyl chains at 77 K indicating ineffective alkyl chain packing between neighboring molecules. Interestingly, inside the clusters, the V-shape appearance for molecule **1** could be identified, i. e. that the hexyl chains are not imaged (Figure 3). Within the clusters, an additional trimeric H-bonding motif consisting of three single H-bonds (two C(2)=O···H(3)–N and one C=O(4)···H(3)–N H-bonds) linking three adjacent bis-uracil units could also be identified (Figure S5, SI). We attribute the complexity of the structure formation observed here to the subtle interplay between the various possible molecule-molecule and molecule-substrate interactions.

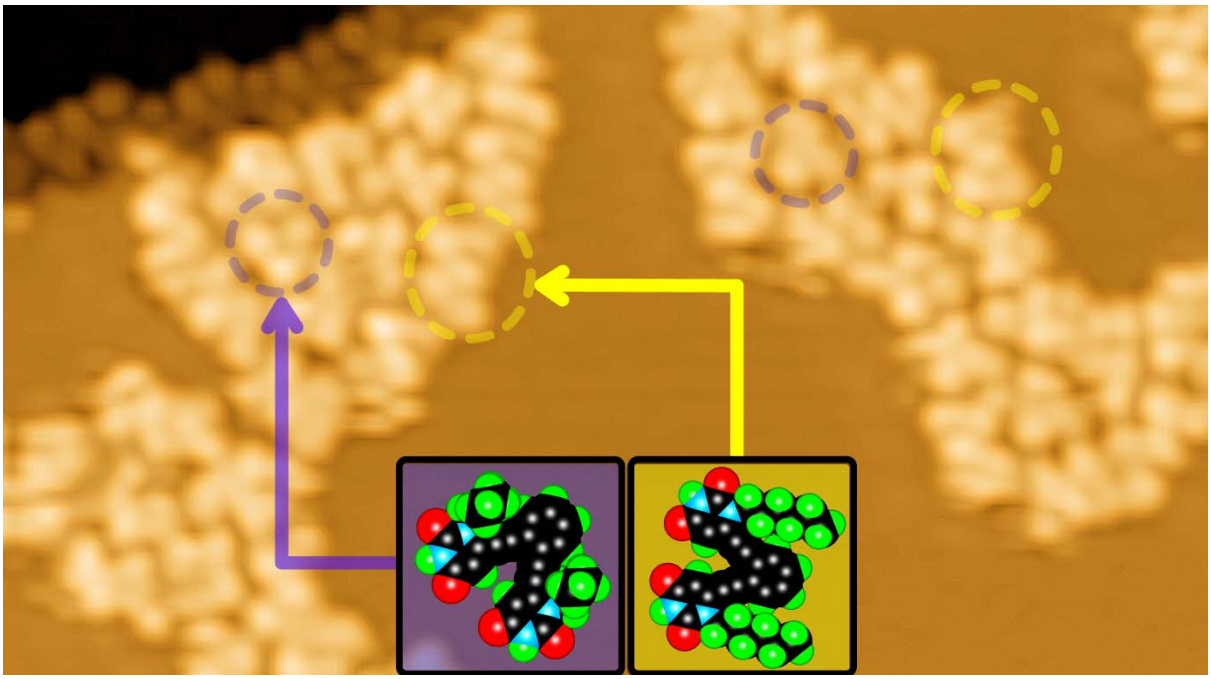

Figure 3. STM image (19 × 11 nm^2, V_t = 0.8 V, I_t = 33 pA) showing the short-range amorphous structures of **1** on Ag(111) for a coverage of ~0.65 ML. Two different configurations (with respect to the alkyl chains configuration) of molecule **1** can be observed. The yellow dashed circle marks a molecule at the edge of a cluster whose alkyl chains are parallel to the metal surface (M-shape appearance); the yellow inset shows the corresponding space filling model for the suggested configuration. The blue dashed circle points towards a molecule within the cluster whose alkyl chains are partly upright. It is assumed that the last four C atoms of the alkyl chain are not in contact with the Ag surface. The three bright protrusions, which are observed in the STM image, are attributed to the aromatic rings while the alkyl chains are not visible (V-shape appearance). The blue inset shows the corresponding space filling model for the suggested configuration.

By further increasing the molecular density on the Ag(111) surface (for coverages between 0.8 ML and 1 ML), a structural phase transformation[32] takes place: the disordered phase "collapses" into a well-ordered 2D close-packed phase (Figure 4). In Figure 4a, the STM image reveals the formation of well-ordered islands. In Figure 4b, within the close-packed arrangement, individual molecules can be identified. Within the close-packed arrangement, similar to the findings for the 2D aggregates, two different appearances were found for the molecules. The terminating molecules (white arrow, Figure 4b) exhibit a M-shape and are imaged as three protrusions (corresponding to the three aromatic rings) and two laterally attached curled wings (corresponding to the hexyl chains), while the molecular units inside the assembly exhibit a V-shape and are imaged only as three bright protrusions with their hexyl chains not being imaged. The ordered pattern consists of parallel rows of molecules **1**. Within one molecular row, the V-

shape molecules point all in the same direction while the direction of the molecules for adjacent rows alternates by 180°.

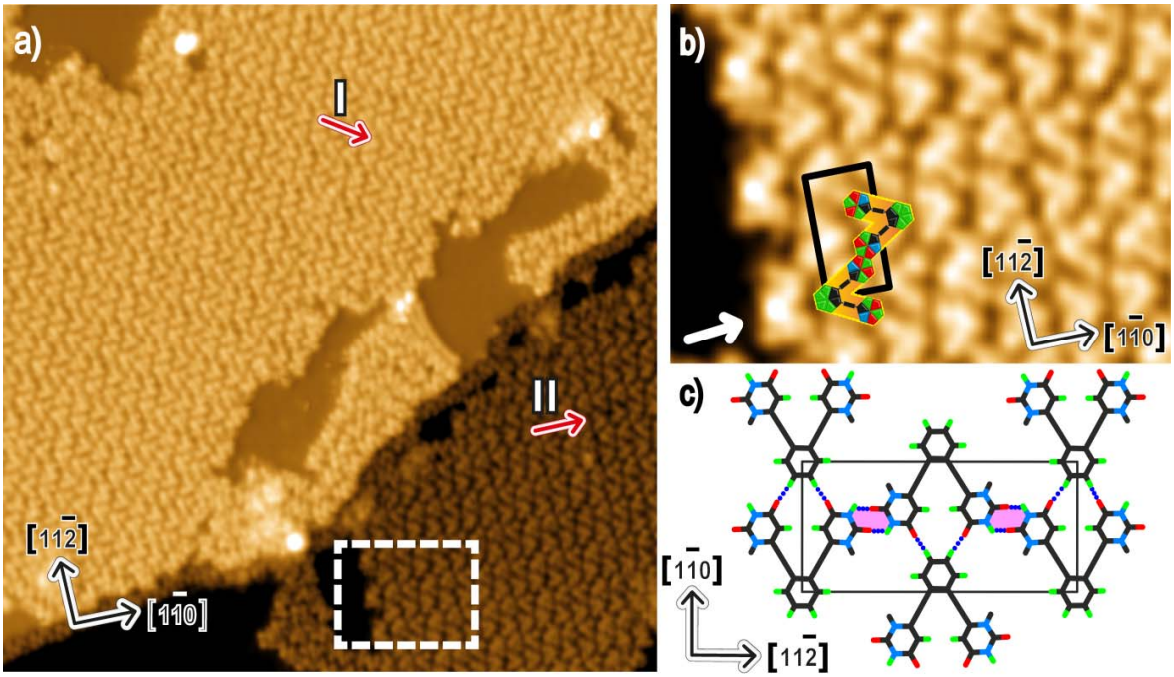

Figure 4. For 0.95 ML, a 2D close-packed arrangement develops on Ag(111). (a) Overview STM image (40 × 40 nm^2, V_t = 1.3 V, I_t = 100 pA) in which two rotational domains of the close-packed assembly marked by red arrows and labeled I and II are visible. (b) Close-up STM image (10 × 7 nm^2) for the area indicated by the white dashed rectangle in (a). The unit cell is indicated by the black rectangle, and schematic representations of two molecules are drawn in to illustrate the molecular arrangement within the assembly. The white arrow points to a molecule located at the island border. It is arranged such that its **U** groups point towards neighboring molecules in order to undergo H-bonding. (c) Tentative molecular model for the arrangement of **1** in the close-packed structure (the alkyl chains are omitted for clarity). The intermolecular H-bonds are shown by blue dashed lines. The unit cell is indicated by the black rectangle. The areas highlighted in pink point to double H-bonds between **U** moieties.

In Figure 4c, the molecular packing within the close-packed arrangement is explained. The intermolecular H-bonds are shown by the dashed blue lines and the hexyl chains were omitted to enhance the visibility. The 2-fold symmetric molecules arrange in a rectangular lattice on the metal surface. From the STM images, the following unit cell parameters are found: (1.1±0.1) × (2.4±0.2) nm^2, α = (90±3)°. There are two molecules per unit cell, and each molecule is involved in 8 H-bonds interacting with four neighbors as follows: along the long side of the unit cell each molecule has both **U** groups involved in double H-bonding; along the short side of the unit cell the O(4) atom of each **U** moiety is involved in a single H-bond with the H atoms of the phenyl ring of a neighboring molecule (C=O(4)···H–C). The fingerprint of the substrate is reflected in the preferential orientation of **1** with respect to the Ag(111) surface. The symmetry axis of **1** follows either the $[1\bar{1}0]$ or $[11\bar{2}]$ high symmetry direction of the underlying substrate. Furthermore, consistent with the substrate's symmetry, rotational domains having an angle of 30° (and multiples thereof) with respect to each other were observed on the surface (in Figure 4a, domains labeled I and II are rotated 30° with respect to each other).

When the molecular models of **1** are overlaid on the STM image of the close-packed arrangement the van der Waals (vdW) radii of the alkyl chains of neighboring molecules overlap. We thus suggest that the alkyl chains partially detach from the surface, with the last four carbon atoms of each hexyl chain lifted from the surface (Figure 3). This has been also found in other surface-confined self-assembled systems.[33-40] In the case of molecule **1** on Ag(111), the molecular geometry with the hexyl chains (partially) detached is attributed to **1** imaged as only three bright protrusions (V-shape appearance). Hence, only by lifting off the alkyl chains it is possible to allow access to the H-bonding interaction sites of the molecules in such a way that the molecules assemble in an ordered pattern driven by **U** dimerization.

Following a thermodynamic approach, we present a qualitative discussion of the phase behavior of the system. Since **1** adsorbed on Ag(111) represents a 2D system, the molecules **1** lost some of their degrees of freedom upon adsorption on the surface as compared with the gas phase (e.g. the degrees of freedom corresponding to the direction perpendicular to the surface are cancelled). In order to gain a better understanding of the factors influencing the phase behavior of **1** on Ag(111), we consider the statistical mechanical expression for entropy. The simplest approach is to use Boltzmann's expression for the entropy of an isolated system of N particles in a volume V at energy E:

$$S = k_B \cdot \ln W \qquad (1)$$

where k_B is Boltzmann's constant and W stands for the total number of accessible states (configurations) of the system.[42] A simple interpretation of the above equation is that W is a measure for the "disorder" in the system. According to Eq. 1, the higher the disorder, the larger the entropy becomes. According to the definition of glasses, which are kinetically frozen-in, nonequilibrium (i.e. non-thermodynamic), amorphous solids,[43] we can associate the disordered phase of **1** on Ag(111) (corresponding to coverages < 0.8 ML) with a glassy phase. When the system is at low temperatures, the dynamic behavior of the molecules on the surface slows down, and at 77 K the system is trapped in a kinetically limited state as can be observed in Figure 1b (see also Figure S2, S3, SI). Only recently, such disordered condensed systems have been characterized on the molecular scale using scanning probe techniques.[44-46]

Molecular self-assembly is a thermodynamically driven process. Therefore, the system (under isobaric and isothermal conditions) can be represented by the Gibbs free energy equation, meaning that a (local) minimum in Gibbs free energy corresponds to a (meta)stable state of the system:

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

where self-assembly is a spontaneous process if ΔG is negative. T, S and H represent temperature, entropy and enthalpy of the system, respectively. Since during our experiments the scanning of the samples always took place at the same temperature (T=constant), three contributions to the free energy of the system (G, whose minimum determines the equilibrium state) must be taken into account: the sum of all interaction energies between the substrate and **1**, the sum of all intermolecular interaction energies, and the total entropy of the molecular layer. According to Eq. 2, in terms of Gibbs free energy, a decrease in entropy has to be compensated by a reduction in enthalpy (adopting a larger but negative value) in order to have $\Delta G < 0$, i.e. mainly through the formation (and optimization) of the molecular bonds due to molecule-substrate and molecule-molecule interactions. In the disordered phase (<0.8 ML), various assembly configurations from molecules **1** were observed. The main responsible factor for this behavior is the presence of the alkyl chains, which - due to their spatial demands - hinder the accessibility of potential H-bonding partners at the **U** moieties (i.e., the homopair formation is hampered). As a consequence, only one **U** moiety per molecule can participate in homopair formation.

By increasing the coverage from 0.8 ML up to 1 ML, the assembly is driven into a well-ordered phase, which corresponds to a state with lower entropy compared with the glassy phase. Only by lifting off the alkyl chains of each molecule it is possible to have access to the H-bonding interaction sites of the molecules **1** in such a way that the intermolecular interactions and the molecule-substrate interactions are optimized. This allows the molecules to assemble in an ordered pattern essentially driven by **U** dimerization. To lift up the chains, the system pays an energetic penalty, which is compensated by the gain in entropy and by minimization of the area

occupied per molecule. All these interactions stabilize the system energetically, and eventually lead to a reduction of Gibbs free energy. In other words, the free energy is minimized through the maximization of both, the number of interactions and molecules per unit area, respectively.

CONCLUSIONS

In this paper, we studied the self-organization of a 2-fold symmetric **U** derivate on Ag(111) as a function of coverage by means of STM under UHV conditions. We found that, by increasing the molecular coverage, a transformation occurs from an ordered to a disordered 2D phase. Specifically, at low and intermediate molecular coverage a glassy phase consisting of 1D chains and 2D aggregates is observed, while close to a first complete molecular layer, a well-ordered 2D close-packed phase forms. The delicate balance of the various molecule-molecule and molecule-substrate interactions is responsible for the complexity of the structure formation. The main driving forces responsible for the structure formations are: (i) the **U** self-complementarity, resulting in **U**-**U** pairs through two C=O(2)···H(3)–N H-bonds and (ii) the steric demands of the alkyl chains. We found that the coverage dependent phase behavior is due to a mutual interplay between entropic (mainly due to the alkyl chains) and enthalpic contributions to the Gibbs free energy of the system, i.e. the system evolves towards a state of lower free energy and higher structural stability.

ASSOCIATED CONTENT

Supporting information.

Additional STM images, experimental methods and synthesis details of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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